

- Johnson, *J. Am. Chem. Soc.* **1994**, *116*, 5722–5729; f) M. G. Finnegan, R. C. Conover, J.-B. Park, Z. H. Zou, M. W. W. Adams, M. K. Johnson, *Inorg. Chem.* **1995**, *34*, 5358–5369; g) J. Zhou, J. W. Raebiger, C. A. Crawford, R. H. Holm, *J. Am. Chem. Soc.* **1997**, *119*, 6242–6250; h) G. Sakane, K. Hashimoto, M. Takahashi, M. Takeda, T. Shibahara, *Inorg. Chem.* **1998**, *37*, 4231–4234; i) R. Hernandez-Molina, V. P. Fedin, M. N. Sokolov, D. M. Saysell, A. G. Sykes, *Inorg. Chem.* **1998**, *37*, 4328–4334; j) B. Rink, M. Brorson, I. J. Scowen, *Organometallics* **1999**, *18*, 2309–2313.
- [3] W. A. Herrmann, A. Egli, E. Herdtweck, R. Alberto, F. Baumgärtner, *Angew. Chem.* **1996**, *108*, 486–489; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 432–434.
- [4] See, for example, a) B. C. Gates, *Chem. Rev.* **1995**, *95*, 511–522; b) K. I. Hadjiivanov, D. G. Klissurski, *Chem. Soc. Rev.* **1996**, 61–69; c) J. Evans, *Chem. Soc. Rev.* **1997**, 11–19; d) A. Hu, K. M. Neyman, M. Stauffer, T. Belling, B. C. Gates, N. Rösch, *J. Am. Chem. Soc.* **1999**, *121*, 4522–4523.
- [5] R. J. Angelici, *Synthesis and Technique in Inorganic Chemistry*, 2nd ed., Saunders, Philadelphia, **1977**, 132–133.
- [6] However, this process is accelerated by heating; for example **4** is 50 % transformed into **1** after 12 h at about 80 °C.
- [7] a) C. Elschenbroich, A. Salzer, *Organometallics: A Concise Introduction*, 2nd ed., VCH, Weinheim, **1992**, p. 230; b) N. L. Armanasco, M. V. Baker, M. R. North, B. W. Skelton, A. H. White, *J. Chem. Soc. Dalton Trans.* **1998**, 1145–1149.
- [8] X-ray structure determination of **5**: Dark green crystals of **5** were obtained by slow crystallization from a saturated solution in hexane. The data were collected on an Enraf Nonius CAD4 diffractometer at room temperature. Intensity measurements were performed by $\omega/2\theta$ scans in the range $3^\circ < \theta < 27^\circ$ on a crystal of dimensions $0.35 \times 0.28 \times 0.23$ mm. Of the 4409 measured reflections, 4193 were independent; largest minimum and maximum in the final difference Fourier synthesis: -1.063 and $1.621 \text{ e } \text{\AA}^{-3}$, $R1 = 0.107$ and $wR2 = 0.296$ (for 2496 reflections with $F > 4\sigma(F)$). The values of $R1$ and $wR2$ are defined as $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR2 = \{[\sum w(F_o^2 - F_c^2)^2] / [\sum w(F_o^2)^2]\}^{1/2}$. The structure was solved by direct methods (SHELXS-97) and refined by least-squares against F^2 (SHELXL-97).^[9] Space groups $P2_1$ and $P2_1/m$ were used to solve and refine the structure, but only the former gave a sensible chemical structure due to disorder in the pentamethylcyclopentadienyl rings and the poor quality of the crystal (unfortunately, data could not be obtained at low temperature). However, this disorder did not affect the location of the core of the molecule. The hydrogen atoms were positioned geometrically and refined by using a riding model. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-134178. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).
- [9] G. M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, Universität Göttingen, Germany, **1997**.
- [10] R. Andrés, M. Galakhov, A. Martín, M. Mena, C. Santamaría, *Organometallics* **1994**, *13*, 2159–2163.
- [11] C. R. Kissinger, E. T. Adman, L. C. Sieker, L. H. Jensen, *J. Am. Chem. Soc.* **1988**, *110*, 8721–8723.
- [12] D. Coucouvanis, S. Al-Ahmad, A. Salifoglou, W. R. Dunham, R. H. Sands, *Angew. Chem.* **1988**, *100*, 1404; *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1353–1355.
- [13] K. J. Haack, R. Goddard, K. R. Pörschke, *J. Am. Chem. Soc.* **1997**, *119*, 7992–7999.
- [14] H. W. Roesky, Y. Bai, M. Noltemeyer, *Angew. Chem.* **1989**, *101*, 788; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 754–755.
- [15] All DFT calculations were carried out with the ADF program^[16] by using triple- ζ and polarization Slater basis sets to describe the valence electrons of C, N, and O. For titanium, a frozen core composed of the 1s, 2s, and 2p orbitals was described by double- ζ Slater functions, the 3d and 4s orbitals by triple- ζ functions, and the 4p orbital by a single orbital. Basis sets of the same quality were used for Cr, Mo, and W. Hydrogen atoms were described by triple- ζ and polarization functions. The geometries and binding energies were calculated with gradient corrections. We used the local spin density approximation, characterized by the electron gas exchange ($X\alpha$ with $\alpha = 2/3$) together with Vosko–Wilk–Nusair parametrization^[17] for correlation. Becke's nonlocal corrections^[18] to the exchange energy and Perdew's nonlocal corrections^[19] to the correlation energy were added. Quasirelativistic corrections were employed by using the Pauli formalism with corrected core potentials. The quasirelativistic frozen core shells were generated with the auxiliary program DIRAC.^[16] In the DFT calculations on complexes **4**–**8**, the methyl groups were replaced by hydrogen atoms.
- [16] a) ADF2.3, Department of Theoretical Chemistry, Vrije Universiteit, Amsterdam; b) E. J. Baerends, D. E. Ellis, P. Ros, *Chem. Phys.* **1973**, *2*, 41–51; c) G. te Velde, E. J. Baerends, *J. Comput. Phys.* **1992**, *99*, 84–98.
- [17] S. H. Vosko, L. Wilk, M. Nusair, *Can. J. Phys.* **1980**, *58*, 1200–1211.
- [18] a) A. D. Becke, *J. Chem. Phys.* **1986**, *84*, 4524–4529; b) A. D. Becke, *Phys. Rev. A* **1988**, *38*, 3098–3100.
- [19] a) J. P. Perdew, *Phys. Rev. B* **1986**, *33*, 7406–7406; b) J. P. Perdew, *Phys. Rev. B* **1986**, *34*, 8822–8824.
- [20] C. S. Bahn, A. Tan, S. Harris, *Inorg. Chem.* **1998**, *37*, 2770–2778.
- [21] The ^{15}N NMR spectrum was referenced to external CH_3NO_2 ($\delta = 0.00$).

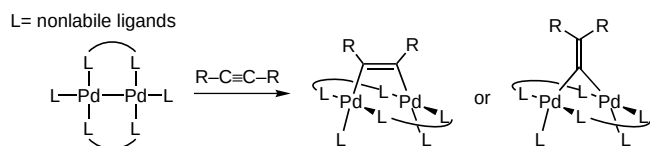
Coupling of Alkynes on a Pd–Pd Bond to Generate an Electrophilic μ -Butenediylidene Moiety**

Tetsuro Murahashi, Toshiaki Otani, Taketoshi Okuno, and Hideo Kurosawa*

In spite of its potential relevance to new palladium-catalyzed reactions, dipalladium(II)-mediated C–C bond-forming reactions have rarely been achieved in a well-defined manner.^[1] This seems curious since the Pd^I–Pd^I complexes are readily accessible and the Pd^{II} and Pd⁰ oxidation states also exist.^[2] One reason could be that relatively nonlabile auxiliary ligands are used to support the Pd–Pd bond (for example, $\text{Ph}_2\text{PCH}_2\text{PPh}_2$, RNC)^[2] so that only a single molecule of unsaturated compounds such as alkynes can be bound (Scheme 1).^[3] We sought Pd–Pd complexes that can provide multiple coordination sites for substrate molecules. We report here a facile, regioselective coupling of a terminal alkyne onto the Pd–Pd bond of $[\text{Pd}_2(\text{PPh}_3)_2(\text{CH}_3\text{CN})_4](\text{PF}_6)_2$ (**1**),^[4] a dipalladium complex with more labile ligands, to generate an electrophilic μ -1 κ C1,4:2 κ C1,4-butenediylidene framework.

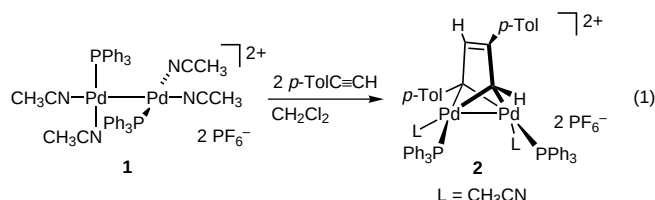
[*] Prof. H. Kurosawa, Dr. T. Murahashi, T. Otani, T. Okuno
Department of Applied Chemistry
Faculty of Engineering, Osaka University
Suita, Osaka, 565-0871 (Japan)
Fax: (+81) 6-6871-7394
E-mail: kurosawa@ap.chem.eng.osaka-u.ac.jp

[**] We thank Prof. Y. Kai and E. Mochizuki (Osaka University) for use of X-ray crystallographic analysis facilities and collection of the data for **2** and **3**. Partial support of this work through Grant-in-Aid for Scientific Research, Ministry of Education, Science and Culture, and CREST of Japan Science and Technology Corporation is gratefully acknowledged. T.M. acknowledges the JSPS research fellowships for young scientists. Thanks are also due to the Analytical Center, Faculty of Engineering, Osaka University for the use of NMR facilities.



Scheme 1. The known reaction patterns of Pd–Pd complexes with alkynes.

The dipalladium(II) complex **1** reacted with two equivalents of *p*-tolylacetylene (*p*-TolC≡CH) immediately at 0 °C in CH₂Cl₂ to give a single product **2** as red crystals in 60% yield after recrystallization from CH₂Cl₂/*n*-hexane [Eq. (1)]. The



reaction was quantitative according to ¹H and ³¹P NMR spectroscopic analysis. The solid-state structure of **2** was determined by X-ray structure analysis (Figure 1) and showed

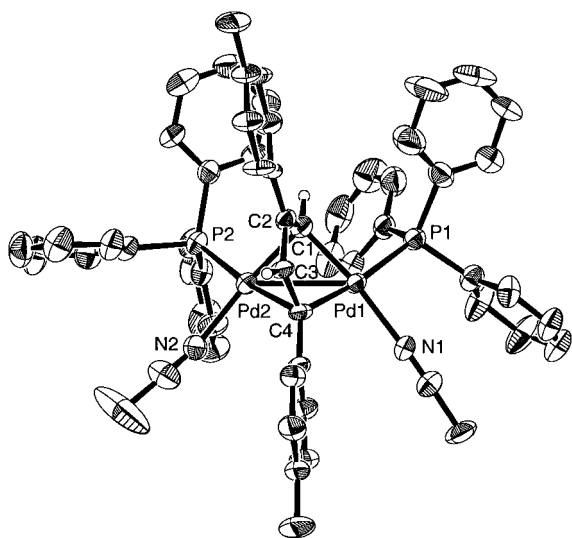
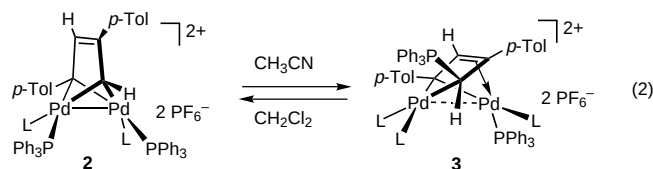


Figure 1. ORTEP plot of **2** (counteranions omitted for clarity). Selected bond lengths [Å] and angles [°]: Pd1–Pd2 2.798(1), Pd1–C1 2.01(1), Pd1–C4 2.06(1), Pd2–C1 2.02(1), Pd2–C4 2.18(1), C1–C2 1.40(2), C2–C3 1.43(2), C3–C4 1.38(2); Pd1–C1–Pd2 87.9(5), C1–C2–C3 109(1), C2–C3–C4 115(1), Pd1–C4–Pd2 82.4(4).

that *p*-tolylacetylene was dimerized in a head-to-tail manner to form a slightly tilted^[5] CHC(Tol)CHC(Tol) bridge across the Pd–Pd bond. The solution ³¹P NMR spectrum of **2** showed only one sharp singlet at δ = 24.96, even at –90 °C, which is consistent with the essentially symmetric bridge structure. Although a number of μ-1κC1,4:2κC1,2,3,4 and μ-1κC1,2,3,4:2κC1,2,3,4 bridging structures of similar C₄ units have been constructed on M–M bonds, the structural characteristics of **2** are rare^[6] and may reflect the carbene-like nature of two terminal carbon atoms coordinated to a 4e acceptor [L₂Pd–PdL₂]²⁺, as in [Pd₂Cl₄(μ-CO)₂]^{2–},^[7] rather than

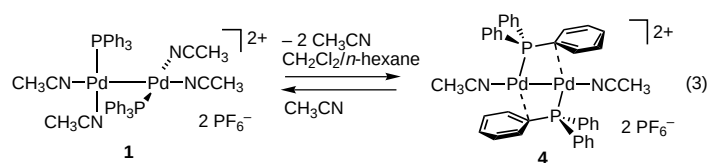
a butadienediyl structure coordinated to a 6e acceptor without a Pd–Pd bond [L₂PdPdL₂]²⁺.^[8] The reaction shown in Equation (1) is in contrast to the oxidative coupling of alkynes to mononuclear Pd⁰ to give palladacyclopentadienes, which is limited to disubstituted activated alkynes such as dimethylacetylene dicarboxylate (DMAD).^[9] Moreover, terminal acetylenes usually undergo oxidative addition of an acetylenic C–H bond to Pd⁰ to give a transient alkynyl palladium hydride complex.^[10]

When **2** was dissolved in CD₃CN the new product **3** was immediately generated quantitatively [Eq. (2)]. A single crystal of **3** suitable for X-ray diffraction analysis was obtained



from CH₃CN/Et₂O. One PPh₃ ligand of **2** migrated to the H-bearing bridging C atom to generate a phosphane ylide complex containing a palladacyclopentenyl moiety.^[11] The ³¹P NMR spectrum of **3** in CD₃CN at –45 °C showed two sets of pairs of doublets with a ratio of 2:1.^[12] Both isomers of **3** were readily converted into **2** in CH₂Cl₂ by loss of a CH₃CN ligand, which means that formation of the ylide is reversible. To our knowledge, such nucleophilic addition at C4 of dinuclear μ-C₄R₄ complexes has not been reported so far in a well-defined manner.

This unique dimerization of an acetylene system may be attributable to the ability of **1** to generate at least two vacant sites on Pd–Pd in solution. This proposal is supported by the facile dissociation of acetonitrile from **1** to give the orange-yellow dipalladium complex **4**, which was isolated in 87% yield on precipitation from a solution of **1** in CH₂Cl₂ [Eq. (3)]. The reverse reaction proceeded in CH₃CN solution.



The X-ray crystal structure of **4** (Figure 2) showed that the two vacant sites generated by loss of two CH₃CN ligands were occupied by η¹-bound^[13] *ipso*-carbon atoms of the PPh₃ phenyl rings (Pd–C_{ipso} 2.336(4) Å).^[14] The distances between Pd1 and the *ortho*-C atoms adjacent to C1 (2.703(4), 2.974(4) Å) are outside the range for Pd–C interaction. No significant structural perturbation of the geometry at the η¹-phenyl or at the phosphorus atom was induced by the μ-1κP:2κC1 coordination,^[15] except that the P–C bond of the coordinated phenyl group (P1–C1 1.832(4) Å) was somewhat longer than those of the uncoordinated phenyl groups (1.801(4), 1.806(4) Å). While triphenylphosphane is one of the most versatile ligands for Pd catalysts, there is no precedent in

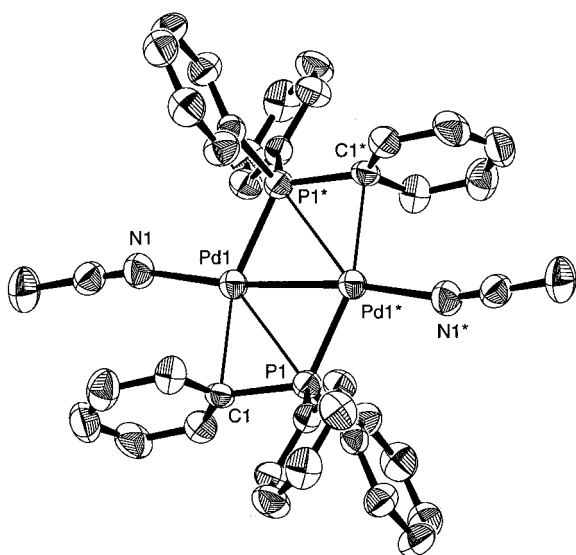
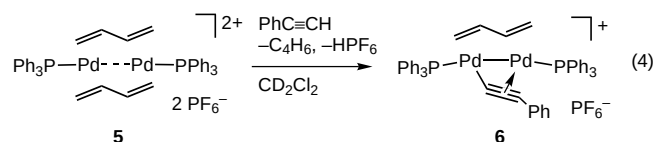


Figure 2. ORTEP plot of **4** (counteranions omitted for clarity). Selected bond lengths [Å] and angles [°]: Pd1–Pd1* 2.5833(7), Pd1*–P1 2.213(1), Pd1–P1 2.753(1), Pd1–C1 2.336(4), P1–C1 1.832(4); Pd1–Pd1*–P1 69.56(3), Pd1*–Pd1–P1 48.87(2), Pd1–P1–C1 57.1(1), P1–C1–Pd1 81.7(1).

which it bridges two Pd centers.^[16] The lability of the PPh₃ bridge of **4** in solution was confirmed by variable-temperature NMR studies. A single set of phenyl carbon signals of the PPh₃ ligands at 23 °C split into two sets with relative intensities of 1:2 at –90 °C, consistent with the coordination and decoordination of the phenyl groups. The fluxional behavior at room temperature could arise from dissociation of *ipso*-C atoms from Pd followed by rotation about the P–Pd bond. Note that **4** reacted with two equivalents of tolylacetylene in CH₂Cl₂ to give **2** in 74 % yield after recrystallization; this represents a simple alkyne coupling on the metal–metal bond without any loss of the auxiliary ligands.

Finally, we also examined the reaction of phenylacetylene with another Pd–Pd complex containing labile bridging ligands, namely, [(μ-1,3-butadiene)₂Pd₂(PPh₃)₂](PF₆)₂ (**5**).^[4] However, instead of an alkyne coupling taking place the quantitative formation of complex **6**, presumably having a μ-1κC1:2κC1,2-alkynyl ligand, occurred in CD₂Cl₂ after 30 min at room temperature with dissociation of one of the 1,3-butadiene ligands [Eq. (4)]. Presumably, the remaining μ-1,3-diene ligand, which would become rather tightly bound^[17]



after the initial exchange between acetylene and the other butadiene ligand of **5**, prohibits either insertion of alkyne into the Pd–Pd bond,^[3] which may represent the initial step of the alkyne coupling in Equation (1), or the coordination of a second molecule of the alkyne.

In summary, alkyne coupling on a Pd–Pd bond yielded an electrophilic butenediylidene species with complete regiose-

lectivity (head-to-tail).^[18] However, the presence of bridging ligands such as 1,3-butadiene prevented dimerization and allowed the formation of a μ-alkynyl ligand.

Experimental Section

2: To an orange solution of **4** (400.0 mg, 0.361 mmol) in CH₂Cl₂ (30 mL) was added dropwise a solution of *p*-tolylacetylene (100.4 μL, 0.721 mmol) in CH₂Cl₂ (5 mL) at 0 °C. After stirring the mixture for 20 min, the resultant red solution was poured into *n*-hexane. Red crystals of **2** (358.1 mg, 74 % yield) were obtained after recrystallization from CH₂Cl₂/*n*-hexane. ¹H NMR (270 MHz, CD₂Cl₂, 25 °C): δ = 8.75 (d, *J* = 3.5 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 2H), 7.41 (d, *J* = 8.4 Hz, 2H), 7.6–7.2 (m, PPh₃, 30H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 5.61 (dt, *J* = 7.80 Hz, *J* = 3.5 Hz, 1H), 2.42 (s, Me, 3H), 2.38 (s, Me, 3H), 1.74 (brs, CH₃CN, 6H); ¹³C NMR (100 MHz, CD₂Cl₂, –60 °C, CH COSY): δ = 196.99 (t, *J* = 60 Hz, C(Tol)-CHC(Tol)CH), 172.84 (s, C(Tol)CHC(Tol)CH), 147.40 (s, C(Tol)-CHC(Tol)CH), 146.06 (s, *p*-Tol), 144.12 (s, *p*-Tol), 139.38 (s, *ipso*-Tol), 133.39 (d, *J* = 13.5 Hz, PPh₃), 131.60 (s, PPh₃), 130.39 (s, C(Tol)-CHC(Tol)CH), 130.10 (s, *m*-Tol), 129.86 (s, *o*-Tol), 129.04 (d, *J* = 10.1 Hz, PPh₃, *m*-Tol), 128.40 (s, *o*-Tol), 127.69 (d, *J* = 47.2 Hz, PPh₃), 126.88 (s, *ipso*-Tol), 123.17 (s, C≡N), 21.67 (s, Me), 21.62 (s, Me), 2.44 (CH₃CN); ³¹P NMR (109 MHz, CD₂Cl₂, 25 °C): δ = 24.76 (s); elemental analysis calcd for C₃₈H₅₂N₂P₄F₁₂Pd₂: C 51.92, H 3.91, N 2.09; found: C 51.71, H 3.84, N 2.12. Crystal data for **2**·2CH₂Cl₂·2H₂O:^[19] C₆₀H₆₀N₂P₄O₂Cl₄F₁₂Pd₂, *M*_r = 1547.68, space group *P* $\bar{1}$ (no. 2), *a* = 14.458(4), *b* = 20.078(4), *c* = 13.703(5) Å, α = 106.49(2), β = 108.28(3), γ = 70.73(2)°, *V* = 3492.58 Å³, *Z* = 2, *F*(000) = 1548, ρ_{calcd} = 1.468 g cm^{–3}, μ(MoKα) = 8.31 cm^{–1}. The data were collected at 223 K on a Rigaku RAXIS CS imaging plate area detector up to 2θ_{max} = 60.0°. The structure was solved by direct methods; 775 variables were refined with 9167 reflections (*I* > 3σ(*I*)) by full-matrix least-squares methods to *R*1 = 0.095 and GOF = 2.32.

3: Orange crystals of **3** were obtained in 87 % yield by crystallization from a solution of **2** in CH₃CN/Et₂O. At ambient temperature all NMR signals were broadened, probably as a result of the interconversion between the isomers on the NMR timescale. Major isomer: ¹H NMR (270 MHz, CD₃CN, –45 °C): δ = 7.9–7.2 (m, PPh₃, 30H), 7.04 (d, *J* = 4.86 Hz, 2H), 6.75 (d, *J* = 7.83 Hz, 2H), 6.51 (d, *J* = 7.83 Hz, 2H), 6.28 (brdd, 1H), 4.54 (d, *J* = 3.51 Hz, 1H); ³¹P NMR (109 MHz, CD₃CN, –45 °C): δ = 31.39 (d, *J* = 25 Hz), 26.37 (d, *J* = 25 Hz). Minor isomer: ¹H NMR (CD₃CN, –45 °C): δ = 3.45 (s, 1H), other signals could not be assigned; ³¹P NMR (CD₃CN, –45 °C): δ = 24.19 (d, *J* = 22 Hz), 20.41 (d, *J* = 22 Hz); elemental analysis calcd for C₆₀H₅₅N₃P₄F₁₂Pd₂: C 52.11, H 4.01, N 3.04; found: C 51.89, H 4.00, N 2.71. Crystal data for **3**·2Et₂O:^[19] C₆₈H₇₅N₃O₂P₄F₁₂Pd₂, *M*_r = 1531.08, space group *P* $\bar{1}$ (no. 2), *a* = 18.72(3), *b* = 18.723(7), *c* = 10.580(4) Å, α = 96.43(3), β = 105.51(6), γ = 90.39(8)°, *V* = 3548(4) Å³, *Z* = 2, *F*(000) = 1560, ρ_{calcd} = 1.433 g cm^{–3}, μ(MoKα) = 6.73 cm^{–1}. The data were collected at 223 K on a Rigaku RAXIS CS imaging plate area detector up to 2θ_{max} = 60.4°. The structure was solved by direct methods; 865 variables were refined with 12340 reflections (*I* > 3σ(*I*)) by full-matrix least-squares methods to *R*1 = 0.104 and GOF = 5.19. The Pd–Pd distance was 2.811(4) Å.

4: Compound **1** (1.300 g, 1.09 mmol) was dissolved in CH₂Cl₂, and the solution poured into *n*-hexane to give orange crystals of **4** (1.052 g, 87 % yield). ¹³C NMR (150 MHz, CD₂Cl₂, 23 °C): δ = 134.98 (s, *p*-Ph), 133.08 (d, *J* = 12.6 Hz, *o*-Ph), 131.44 (d, *J* = 11.6 Hz, *m*-Ph), 119.90 (s, C≡N), 116.29 (brs, *ipso*-Ph), 2.96 (s, Me); ³¹P NMR (162 MHz, CD₂Cl₂, 25 °C): δ = 23.13 (s); elemental analysis calcd for C₄₀H₃₆N₂P₄F₁₂Pd₂: C 43.30, H 3.27, N 2.52; found: C 43.15, H 3.28, N 2.43; ESI-MS for C₄₀H₃₆N₂P₄F₆Pd₂: calcd: 964.49, found: 964.5; ¹³C NMR (162 MHz, CD₂Cl₂, –90 °C, Ph* indicates coordinated Ph): δ = 136.83 (s, *p*-Ph*), 133.90 (d, *J* = 12.6 Hz, *o*-Ph), 133.50 (s, *m*-Ph*), 132.83 (s, *p*-Ph), 129.04 (d, *J* = 11.5 Hz, *m*-Ph), 127.31 (s, *o*-Ph*), 126.02 (d, *J* = 55.3 Hz, *ipso*-Ph), 118.31 (s, C≡N), 92.11 (d, *J* = 49.5 Hz, *ipso*-Ph*), 2.94 (s, Me). Crystal data for **4**:^[19] C₄₀H₃₆N₂P₄F₁₂Pd₂, *M*_r = 1109.41, space group *P* $\bar{1}$ (no. 2), *a* = 11.045(2), *b* = 12.434(2), *c* = 8.354(2) Å, α = 90.92(2), β = 92.94(2), γ = 110.95(1)°, *V* = 1069.3(4) Å³, *Z* = 1, *F*(000) = 550, ρ_{calcd} = 1.723 g cm^{–3}, μ(MoKα) = 10.60 cm^{–1}. The data were collected at 296 K on a Rigaku AFC5R diffractometer up to 2θ_{max} = 55.1°. The structure was solved by Patterson methods; 271 variables were

refined with 4171 reflections ($I > 3\sigma(I)$) by full-matrix least-squares methods to $R1 = 0.049$, $R_w = 0.036$ and $GOF = 3.03$.

6: Phenylacetylene (14.5 μL , 0.132 mmol) was added to a yellow suspension of **5** (100.0 mg, 0.0881 mmol) in benzene and the solution stirred for 5 min at room temperature. Then pyridine (7.1 μL , 0.0881 mmol) was added, and the mixture was stirred for 10 min. The resultant orange solution was filtered, and the filtrate was poured into *n*-hexane to afford **6** as a yellow powder (63.7 mg, 70% yield). The NMR spectra of the reaction mixture in CD_2Cl_2 confirmed quantitative formation of **6** without addition of pyridine. ^1H NMR (400 MHz, CD_2Cl_2 , 25 °C): $\delta = 7.6\text{--}7.4$ (m, PPh_3 , 30H), 7.00 (t, $J = 7.6$ Hz, 1H), 6.80 (t, $J = 7.6$ Hz, 2H), 6.59 (d, $J = 7.6$ Hz, 2H), 3.67 (brs, 2H), 3.02 (brs, 2H), 2.79 (brd, 2H); ^{31}P NMR (162 MHz, CD_2Cl_2 , 25 °C): $\delta = 33.8$ (s); elemental analysis calcd for $\text{C}_{48}\text{H}_{41}\text{P}_3\text{F}_6\text{Pd}_2$: C 55.56, H 3.98; found: C 55.35, H 4.03; Raman (solid): $\tilde{\nu}_{\text{C}\equiv\text{C}} = 2008, 1975\text{ cm}^{-1}$; the fluxional nature of **6** at 25 °C was confirmed by variable-temperature NMR analyses; ^1H NMR (400 MHz, CD_2Cl_2 , -80°C): $\delta = 7.6\text{--}7.4$ (m, 30H), 6.94 (t, 1H), 6.75 (t, 2H), 6.48 (d, 2H), 4.14 (brd, 1H), 3.71 (brm, 1H), 3.19 (brd, 1H), 3.05 (brs, 1H), 2.22 (brm, 2H); ^{31}P NMR (162 MHz, CD_2Cl_2 , -80°C): $\delta = 35.2$ (d, $J = 51.8$ Hz), 32.7 (d, $J = 51.8$ Hz).

Received: June 2, 1999 [Z13510]

- [1] S. J. Young, B. Kellenberger, J. H. Reibenspies, S. E. Himmel, M. Manning, O. P. Anderson, J. K. Stille, *J. Am. Chem. Soc.* **1988**, *110*, 5744, and references therein.
- [2] P. M. Maitlis, P. Espinet, M. J. H. Russel in *Comprehensive Organometallic Chemistry*, Vol. 6 (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon, **1982**, chap. 38.3.
- [3] a) C.-H. Lee, C. T. Hunt, A. L. Balch, *Inorg. Chem.* **1981**, *20*, 2498; b) H. Werner, P. Thometzek, K. Zenkert, R. Goddard, H.-J. Kraus, *Chem. Ber.* **1987**, *120*, 365; c) S. J. Higgins, B. L. Shaw, *J. Chem. Soc. Dalton Trans.* **1988**, 457; d) J. A. Davies, K. Kirshbaum, C. Kluwe, *Organometallics* **1994**, *13*, 3664; e) T. R. Jack, C. J. May, J. Powell, *J. Am. Chem. Soc.* **1977**, *99*, 4707.
- [4] T. Murahashi, T. Otani, E. Mochizuki, Y. Kai, H. Kurosawa, S. Sakaki, *J. Am. Chem. Soc.* **1998**, *120*, 4536. We also found that **1** can be easily prepared from $[\text{Pd}(\text{PPh}_3)_2(\text{CH}_3\text{CN})_2](\text{PF}_6)_2$ and 0.5 equiv of $[\text{Pd}_2(\text{dba})_3]$ (dba = *trans,trans*-dibenzylideneacetone) in $\text{CH}_3\text{CN}/\text{CH}_2\text{Cl}_2$ in 70% yield of isolated product.
- [5] The slight tilting of the C_4 framework results in an angle of 74.5° between the C1-C2-C3-C4 mean plane and the Pd1-Pd2 vector.
- [6] Acetylene coupling on metal-metal bonds of middle transition metals has been reported; $\mu\text{-}1\kappa\text{C1,2,3,4:}2\kappa\text{C1,2,3,4}$ type: a) Q. Feng, M. L. H. Green, P. Mountford, *J. Chem. Soc. Dalton Trans.* **1992**, 2171; $\mu\text{-}1\kappa\text{C1,4:}2\kappa\text{C1,2,3,4}$ -type: b) S. A. R. Knox, R. F. D. Stansfield, F. G. A. Stone, M. J. Winter, P. Woodward, *J. Chem. Soc. Dalton Trans.* **1982**, 173; c) M. H. Chisholm, K. Folting, J. C. Huffman, I. P. Rothwell, *J. Am. Chem. Soc.* **1982**, *104*, 4389, and references therein; d) Review: W. P. Fehlhammer, H. Stolzenberg in *Comprehensive Organometallic Chemistry*, Vol. 4 (Eds.: G. Wilkinson, F. G. A. Stone, E. W. Abel), Pergamon, **1982**, chap. 31.4; A similar complex $[(\mu\text{-}1\kappa\text{C1,4:}2\kappa\text{C1,4-CHC(Ph)C(Ph)CH)Ni}_2(\text{depe})_2](\text{PF}_6)_2$ (depe = 1,2-bis(diethylphosphanyl)ethane) was derived from a butadienediyl Ni^{II} complex without any evidence of acetylene coupling on the Ni-Ni bond: e) C. J. Lawrie, H. E. Dankosh, B. K. Carpenter, *J. Organomet. Chem.* **1991**, *411*, C7; $[(\mu\text{-}1\kappa\text{C1,4:}2\kappa\text{C1,4-CHC(CH}_2\text{OH)C(CH}_2\text{OH)-CH)Ni}_2(\text{diimine})_2]$, which has a different formal valency of the metal centers from **3**, has also been structurally characterized: f) R. Diercks, L. Stamp, J. Kopf, H. tom Dieck, *Angew. Chem.* **1984**, *96*, 891; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 893.
- [7] N. M. Kostić, R. F. Fenske, *Inorg. Chem.* **1983**, *22*, 666.
- [8] According to a calculation $\mu\text{-}1\kappa\text{C1,4:}2\kappa\text{C1,2,3,4}$ -bridging bonding is more stable than $\mu\text{-}1\kappa\text{C1,4:}2\kappa\text{C1,4}$ bonding to the 6e acceptor $\text{Fe}_2(\text{CO})_6$; D. L. Thorn, R. Hoffmann, *Inorg. Chem.* **1978**, *17*, 127.
- [9] a) K. Moseley, P. M. Maitlis, *J. Chem. Soc. Dalton Trans.* **1974**, 169; b) R. van Belzen, R. A. Klein, H. Kooijman, N. Veldman, A. L. Spek, C. J. Elsevier, *Organometallics* **1998**, *17*, 1812.
- [10] a) G. A. Chukhadzhyan, Z. K. Evoyan, L. N. Melkonyan, *Zh. Obshch. Khim.* **1975**, *45*, 1114; b) F. Schager, W. Bonrath, K.-R. Pörschke, M. Kessler, C. Kürger, K. Seevogel, *Organometallics* **1997**, *16*, 4276, and references therein.
- [11] Metallacyclopentenyl complexes derived from acetylenes are very rare: H. Yamazaki, K. Yasufuku, Y. Wakatsuki, *Organometallics* **1983**, *2*, 726.
- [12] The exact structure of the minor isomer was not identified. It may arise from exchange of PPh_3 ligand with one of the three acetonitrile ligands of the major isomer; the two isomers interconvert rapidly at room temperature (see Experimental Section).
- [13] A limited number of η^1 -benzene complexes have been reported: a) R. A. Bartlett, H. Chen, P. P. Power, *Angew. Chem.* **1989**, *101*, 325; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 316; b) L. R. Falvello, J. Fornies, R. Navarro, V. Sicilia, M. Tomás, *Angew. Chem.* **1990**, *102*, 952; *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 891; c) L. R. Falvello, J. Fornies, R. Navarro, V. Sicilia, M. Tomás, *J. Chem. Soc. Dalton Trans.* **1994**, 3143; d) P. Braunstein, U. Englert, G. E. Herberich, M. Neuschütz, *Angew. Chem.* **1995**, *107*, 1090; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1010.
- [14] $[\text{Pd}_2(\text{dppp})_2]^{2+}$ (dppp = 1,3-bis(diphenylphosphanyl)propane) has a similar *ipso*-phenyl coordination structure: P. H. M. Budzelaar, P. W. N. M. van Leeuwen, C. F. Roobeek, A. G. Orpen, *Organometallics* **1992**, *11*, 23.
- [15] For example, the η^1 -coordinated phenyl ring maintained its aromaticity ($\text{C-C } 1.361(7)\text{--}1.398(5)\text{ \AA}$) and planarity, whereby P1 also lies on the same plane. The C1-P1-Pd1 angle of $118.5(1)^\circ$ is in the usual range for coordinated phosphane ligands.
- [16] The only example of a triphenylphosphane bridge across trinuclear Pd-Pd-Pd was recently found in $[\text{Pd}_3(\mu_3\text{-}1\kappa\text{P:}2\kappa\text{C1,2:}3\kappa\text{C3,4-PPh}_3)_2(\text{PPh}_3)_2]^{2+}$: a) S. Kannan, A. J. James, P. R. Sharp, *J. Am. Chem. Soc.* **1998**, *120*, 215; $\mu\text{-}1\kappa\text{P:}\eta^1\text{-PPh}_3$ ($x = 2,4,6$) coordination was observed with other transition metals: b) G. B. Robertson, P. O. Whimp, *J. Organomet. Chem.* **1973**, *60*, C11; c) R. Luck, R. H. Morris, J. F. Sawyer, *Organometallics* **1984**, *3*, 1009; d) H.-F. Hsu, S. R. Wilson, J. R. Shapley, *Organometallics* **1997**, *16*, 4937; e) I. Ara, L. R. Falvello, J. Fornies, E. Lalinde, A. Martín, F. Martínez, M. T. Moreno, *Organometallics* **1997**, *16*, 5392.
- [17] The μ -butadiene ligand in the monobutadiene complex $[\text{Pd}_2(\mu\text{-}1,3\text{-butadiene})(\mu\text{-Cl})(\text{PPh}_3)_2]^{+4}$ is much less labile than that of **5**.
- [18] Products analogous to **2** were obtained when $p\text{-X-C}_6\text{H}_4\text{C}\equiv\text{CH}$ ($\text{X} = \text{H}, \text{Cl}$) were used (36–56% yield according to NMR spectroscopy; relatively low yields were partly a result of decomposition of the products). Inner alkynes such as $\text{PhC}\equiv\text{CPh}$ and $\text{PhC}\equiv\text{CMe}$ also reacted with **1** or **4**, but more complicated results were obtained under the reaction conditions of Equation (1).
- [19] Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-124471 (**2**), -124472 (**3**), and -124473 (**4**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).